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- (54) Surface Treated, Electrically Resistive Metal Foil for Production of Printed Electrical Resistors  
(57) A cupronickel foil of high resistivity has a micro-rough codeposit containing copper and nickel electrodeposited on a surface thereof to produce a foil which can be strongly bonded to a resinous substrate by heat-bonding or by means of an adhesive. The cupronickel foil is conveniently of 55% copper and 45% nickel. A laminate of the foil on a substrate finds particular application where the laminate is to be used in an aggressive environment which can cause delamination of conventional laminates of resistor foil.

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SPECIFICATION  
Electrically Resistive Metal Foil

This invention relates to the production of electrically resistive metal foil. More specifically, the invention provides a method for the treatment of metallic foil used in the production of printed electrical resistors to improve the bond strength of the foil to a supporting substrate. The invention also 5 provides such treated foil.

A widely used electrically resistive foil is produced commercially by rolling down a billet of a cupronickel alloy. The foil thus produced has very smooth surfaces and can be attached to a substrate, using an adhesive, only with difficulty to produce a laminate of erratic and low bond strength. In 10 addition, certain of the adhesives used in such applications are degraded by organic liquids and vapours. Resistors produced from such laminates cannot, therefore, be used in environments where exposure to such liquids and vapours could occur as this would normally cause delamination of the foil 15 from the substrate.

British Patent No. 951,660 relates to the adhesion of an electrically resistive metal foil to a resinous substrate for use in the production of printed resistors. The process there described involves 15 the steps of degreasing the foil, etching a surface with ferric chloride and then bonding the etched face of the foil to a substrate by means of an interposed layer of adhesive.

In the production of electrically conductive foils of copper for use in the manufacture of printed circuits it is not uncommon practice to provide a micro-rough surface on one face of the foil to permit 20 keying of the foil to a substrate by means of adhesive. Such a roughened surface is usually produced electrolytically either during manufacture of the foil by electrodeposition of the copper or afterwards by electrolytic deposition of one or more layers on the surface. Our British Patent Application No. 1,413,494 (U.S. Patent No. 3,918,926) describes one such process of after-treatment of conductive copper foil to produce a rough surface of dentritic micro-structure.

25 An object of the present invention is to obviate or mitigate the aforesaid disadvantages of known electrically resistive foils.

According to the present invention there is provided an electrically resistive foil comprising a foil of a cupronickel alloy of high resistivity having on a surface thereof an electrolytically deposited micro-rough film containing copper and nickel.

30 The invention also provides a method of producing electrically resistive foil comprising providing a foil of cupronickel alloy and electrolytically codepositing on a surface of the foil a micro-rough film containing copper and nickel.

The cupronickel foil is preferably composed of an alloy of 55% copper and 45% nickel. This alloy has a temperature coefficient of resistance which makes it particularly desirable for the production of 35 temperature-stable resistors over the range of from zero to 100°C. The specific resistance (resistivity) of the alloy is preferably from 48 to 52  $\mu$  ohms/cm<sup>3</sup>.

The optimum concentration of the electrolyte for deposition of the film of codeposit is as follows:

1 to 6 grams/litre nickel (as metal)	40
0.3 to 0.6 grams/litre copper (as metal)	40
50 to 100 grams/litre ammonium sulphate	40
10 to 40 grams/litre boric acid	40

This electrolyte is preferably adjusted to a pH of 2.5 with dilute sulphuric acid. the deposition is 45 preferably carried out at a temperature of from 20 to 50°C and at a current density of from 20 to 80 amps/square foot for from 5 to 25 seconds, using a lead anode. the nickel and copper are normally added to the electrolyte in the form of their sulphates.

The concentration of the various components of the bath may be varied over wide ranges. Nickel may be in the concentration range of from 0.5 to 10 grams/litre and copper from 0.2 to 2 grams/litre. the atomic ratio Ni:Cu is desirably maintained between 1:1 and 16:1. The higher ratio produces a more metallic deposit; whilst the lower ratio produces a more powdery deposit. The optimum range is from 50 6:1 to 10:1.

The copper content of the co-deposit generally varies between 1 and 10%, whilst within the preferred range it more suitably lies between 3 and 6%. However, the ratio of the metals in the electrodeposit is not in direct relationship with the ionic concentration of the metal ions in the electrolyte.

55 Ammonium sulphate may be present in the bath as a current carrier and its concentration may range between 10 and 200 grams/litre, depending on the required conductivity.

The boric acid is merely a pH buffer and may range between 10 and 40 grams per litre.

The pH of the electrolyte may lie between 2.0 and 4.0. Deposition ceases at a low pH, whereas the deposit becomes very powdery at high pH. The most preferred value is 2.5 pH.

60 The temperature of the electrolyte may be varied from 20 to 80°C. At higher temperatures the deposit becomes more metallic in nature, however it is possible to increase the concentration of the pH buffer with the use of higher temperatures and so increase the pH stability.

The criterion for judging the acceptability of the deposited film is that its presence on the cupronickel foil should not greatly alter the resistance of the foil. This means, in practice, that the resistivity of the deposited film should be higher than that of the foil so that in use current, taking the path of least resistance, travels through the foil and not the deposited film. Deposition from an electrolyte having a composition within the ranges defined above will ensure that such criterion is satisfied when the deposit is very thin (less than 4 microns).

However, the criterion mentioned in the previous paragraph for judging the acceptability of the deposited film has to be reconciled to the physical requirements for the film. It may be possible for example to deposit a film which satisfies the requirements for resistance but which is powdery and non-adherent or bright and metallic in nature and which would lead to very low and unacceptable bond strengths, or at worst delamination of the foil from the substrate. It is, therefore, desirable to work within comparatively narrow limits of nickel-copper ratios and ionic metal concentrations coupled with the choice of current density and plating time to ensure that the product not only has acceptable electrical resistance but also satisfies the physical requirements which would enable it to be bonded strongly to a substrate.

The current density may be varied between 10 and 100 amps/square foot, the plating time being selected from within the range of from 5 to 50 seconds. Thus the choice of a higher current density requires a shorter plating time to obtain a deposit to suit the physical requirements. Also the resultant deposit thickness from the use of these conditions will have no effect on the resistance of the foil.

Taking the foregoing considerations into account the preferred operating conditions for the process are as follows:

Atomic ratio Ni:Cu from 6:1 to 10:1

Current Density from 20 to 80 amps/square foot

Temperature from 20 to 50°C

Plating Time from 5 to 25 seconds

The particular apparatus used to deposit the nickel/copper film to the foil forms no part of the present invention but the film can be most conveniently deposited by passing the foil through an electrolyte adjacent to plate anodes, the foil being passed in serpentine fashion in proximity to the anodes. By appropriate contact between the foil and the conducting rollers the foil is made cathodic in the circuit. By passing the foil through such a system in such a manner that the surface to be coated faces the active face of the anodes the copper/nickel film will be deposited on that face.

The method of the invention may include one or more pretreatment steps designed to make the surface of the foil receptive to the film to be deposited thereon. Preferably the pretreatment includes, sequentially, a degreasing step in which the foil is simply washed in hot water containing an alkaline cleaner, an electrolytic cleaning step in which the foil is made cathodic in an aqueous solution of the same alkaline cleaner, and an acid dip step in which the foil is passed through a bath of aqueous acid such as 20% sulphuric or hydrochloric acid. Water washing may be effected between the steps and particularly between the acid dip and the electrolytic deposition.

The foil of the invention may be bonded to certain resinous substrates without an intermediate adhesive: it is not possible to do this with untreated foils. For certain other substrates an adhesive is necessary but the foil of the invention exhibits improved bond strengths over those obtainable with untreated foil. For the manufacture of resistors, epoxy resin-impregnated glass-fibre boards are preferred and to these the foil of the invention may be bonded without adhesive. The product thus is unaffected by organic solvent vapours. Both flexible and non-flexible supports such as Teflon-impregnated fibreglass ('Teflon' is the Trade Mark for polytetrafluoroethylene), Kel-F impregnated fibreglass ('Kel-F' is a Trade Mark for certain fluorocarbon products including polymers of trifluorochloroethylene and certain copolymers) and the like are also usable. Other flexible substrates include polyimides such as those known under the designation 'Kapton' and 'H-film' (both are manufactured by duPont and are polyimide resins produced by condensing a pyromellitic anhydride with an aromatic diamine).

The adhesives used to bond the treated foil to the substrate are those conventionally used for the specific application in question. "FEP" (a fluorinated ethylene propylene resin in the form of a copolymer of tetrafluoroethylene and hexafluoropropylene having properties similar to Teflon) being particularly appropriate for the Teflon and Kel-F and conventional epoxy resins being useful for the other materials. The method of bonding the foil to the substrate is conventional and forms no part of the present invention, typical details of such bonding being set forth for example in the U.S. Pat. No. 3,328,275 to Waterbury.

The invention will now be described by way of illustration in the following Example.

#### Example

A series of seven tanks was provided for the performance of the treatment sequence to be described. The foil to be treated was passed from tank to tank in serpentine fashion, the residence time in each tank being determined by the speed of the foil.

A cupronickel foil of 55% copper, 45% nickel (Ferry, Trade Mark) was subjected to the following treatments in sequence:

1) *Degreasing* in a hot (90°C) aqueous solution of an alkaline detergent for 2 minutes. The detergent was a commercial product sold under the Trade Mark R.S.K.

5 2) *Electrolytic Cleaning* in a solution of the same detergent as in step 1 at 50 to 60°C for 30 seconds, the foil being made cathodic at a current density of 50 amps/sq. ft. using mild steel anodes.

3) *Water Wash*

4) *Acid Dip* The foil was immersed in 20% aqueous sulphuric acid at 25°C for 30 seconds.

5) *Water Wash*

10 6) *Electrolysis* The electrolyte composition and operating conditions were as follows:

Nickel	4 grams/litre
Copper	0.5 grams/litre
Ammonium sulphate	50 grams/litre
Boric acid	10 grams/litre
pH	2.5
Time	15 seconds
Temperature	25°C
Current Density	50 amps/sq. ft.
Anodes	Lead

20 7) *Water Wash*

8) *Drying*

Foil treated in the above manner was tested for improvement in bond strength.

Untreated foil (for comparison), lightly treated foil (plated for 10 seconds) and normally treated foil (plated for 15 seconds) were bonded to an epoxy resin-impregnated glass-fibre substrate.

25 Further samples were coated with a polyvinylbutyl modified phenolic adhesive to form a coating of between 20 and 30 grams/square metre prior to bonding to the same substrate above.

The following bond strength results were obtained.

	<i>Uncoated</i>	<i>Adhesive coated</i>	
30 Untreated foil	1.0 lbf/in	4.6 lbf/in	
Lightly treated foil	3.6 lbf/in	9.2 lbf/in	
Normally treated foil	4.8 lbf/in	10.0 lbf/in	30

There was no change in the resistance of the foil after treatment.

#### Claims

1. Electrically resistive foil comprising a foil of a cupronickel alloy of high resistivity having on a surface thereof an electrolytically deposited micro-rough film containing copper and nickel.

35 2. Foil as claimed in claim 1, in which the cupronickel alloy consists of 55% by weight of copper and 45% by weight of nickel.

3. Foil as claimed in claim 1 or claim 2, in which the resistivity of the cupronickel alloy is from 48 to 52  $\mu$  ohms/cm<sup>3</sup> and the resistivity of the electrolytically deposited film is higher than that of the said alloy.

40 4. Electrically resistive foil, according to claim 1, substantially as hereinbefore described.

5. A method of producing electrically resistive foil comprising providing a foil of cupronickel alloy and electrolytically codepositing on a surface of the foil a micro-rough film containing copper and nickel.

45 6. A method as claimed in claim 5, in which the cupronickel alloy consists of 55% by weight of copper and 45% by weight of nickel.

7. A method as claimed in claim 5 or claim 6, in which the electrolytic deposition is effected from an electrolyte containing, in aqueous solution, from 0.5 to 10 grams/litre of nickel and from 0.2 to 2 grams/litre of copper, the atomic ratio of nickel to copper being from 1:1 to 16:1.

50 8. A method as claimed in claim 7, in which the atomic ratio of nickel to copper is from 6:1 to 10:1.

9. A method as claimed in claim 7 or claim 8, in which the electrolyte also contains from 10 to 200 grams/litre of ammonium sulphate as a current carrier.

55 10. A method as claimed in claim 7 or 8 or 9, in which the electrolyte contains from 1 to 6 grams/litre of nickel (as metal); from 0.3 to 0.6 grams/litre of copper (as metal); from 50 to 100 grams/litre of ammonium sulphate and from 10 to 40 grams/litre of boric acid.

11. A method as claimed in any of claims 7 to 10, in which the electrolyte additionally contains sufficient sulphuric acid to give a pH of from 2.0 to 4.0.

60 12. A method as claimed in claim 11, in which the pH is 2.5.

13. A method as claimed in any of claims 7 to 12, in which the nickel and copper are added to the electrolyte in the form of their sulphates.

14. A method as claimed in any of claims 7 to 13, in which the electrodeposition is effected at an electrolyte temperature of from 20 to 80°C and at a current density of from 10 to 100 amps/square foot for from 5 to 50 seconds, using a lead anode.

15. A method as claimed in claim 14, in which the temperature is from 20 to 50°C, the current density is from 20 to 80 amps/square foot and the time period from 5 to 25 seconds. 5

16. A method of producing electrically resistive foil, according to the Example hereinbefore.

17. A method of producing electrically resistive foil, as claimed in claim 5, substantially as hereinbefore described.

18. Electrically resistive foil whenever produced by the method claimed in any of claims 5 to 17.

19. An electrical resistor comprising a non-conductive laminar substrate having thereon an electrically resistive foil as claimed in claim 1, 2, 3 or 18. 10

20. A resistor as claimed in claim 19, in which the foil is bonded to the substrate by means of an interposed layer of adhesive.

21. A resistor as claimed in claim 19, in which the substrate is of synthetic resinous material and the foil is bonded thereto by the application of heat and pressure. 15

22. A resistor as claimed in claim 19, substantially as hereinbefore described.

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Synthetic high polymers  
organic compound.